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A SIGNIFICANT UPPER LIMIT FOR THE RATE OF FORMATION OF OCS FROM THE REACTION OF OH WITH CS_2

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Abstract. The rate of reaction of OH with CS_2 to form OCS by reaction (1) has been measured through observation of $O^{14}CS$ following 254 nm photolysis of mixtures of H_2O_2 with $^{14}CS_2$. The OH concentrations have been monitored through simultaneous measurement in the same cell of either (a) the oxidation of CO to CO_2, or (b) the removal of a hydrocarbon such as C_3H_8 or iso-C_4H_{10}. The upper limit for the formation of OCS based on (a) corresponds to a rate constant $k_1 < 0.3 \times 10^{-14}$ cm^3 $molecule^{-1}$ sec^{-1}. Other chemical reactions in the system have led to the formation of both ^{14}CO and $^{14}CO_2$, indicating the existence of a complex combination of reactions such that the observed $O^{14}CS$ need not have been formed by (1).

The rate of reaction (1) is sufficiently slow that it is neither an important atmospheric sink for CS_2 nor an important source for atmospheric OCS. The reaction of OH with OCS has not been measured in these experiments, but by analogy with k_1 it is probably not an important atmospheric sink for OCS nor an important source of SO_2.

Introduction

The discovery that both CS_2 (Sandalls and Penkett, 1977) and OCS (Hanst et al., 1975; Maroulis et al., 1977) are present in tropospheric air at the level of $\sim 10^{-10}$ by volume has produced considerable interest in both their sources and sinks (Crutzen, 1976; Sze and Ko, 1979a,b; Logan et al., 1979; Rowland, 1979; Turco et al., 1980). Neither of these compounds undergoes direct solar photodecomposition in the troposphere, although CS_2 does absorb in the near ultraviolet region between 290-380 nm. However, a recent report of rapid, homogeneous gas phase reactions of these molecules with OH radicals (Kurylo, 1978) would represent an important tropospheric sink for each if the report were correct. Kurylo has proposed the reaction mechanisms in (1) and (2) to explain these laboratory observations.

$$OH + SCS \rightarrow S(OH)-C-S \rightarrow OCS + SH \quad (1)$$

$$OH + OCS \rightarrow O(OH)-C-S \rightarrow OCO + SH \quad (2)$$

In the absence of any product analysis, the proposed attack of OH on OCS could also be attributed to the simpler, approximately thermoneutral abstraction reaction (3), but the corresponding attack of OH on CS_2 in (4) is endothermic by more than 20 kcal/mole, and cannot be a fast reaction at the temperature of the measurements (298K). Since the reaction mechanisms for OH reaction are likely to be similar for CS_2 and OCS, the alternate reaction paths of (1) and (2) have been postulated, involving a more complex type of intermediate whose rearrangement ultimately leads to the exothermic formation of SH radicals (Kurylo, 1978; Kurylo and Laufer, 1979; Cox and Sheppard, 1980). If the rate constants measured for OH disappearance in these systems can be correctly assigned to (1) and (2), then the tropospheric attack of OH on CS_2 is both an important sink for CS_2 and an important source of OCS, and the attack of OH on OCS is an important sink for it and an important precursor reaction for the formation of SO_2 in the troposphere (Sze and Ko, 1979a, b; Logan et al., 1979).

$$OH + OCS \rightarrow HOS + CO \quad (3)$$

$$OH + SCS \rightarrow HOS + CS \quad (4)$$

The reported values of the rate constant for OH reaction with CS_2 show little agreement with one another, as summarized in Table 1. Comparable disagreement exists for the measurements of the rate constant for OH reaction with OCS (Kurylo, 1978; Atkinson et al., 1978; Wine, Shah and Ravishankara, 1980). In most of these studies, evidence has been sought only for the rate of disappearance of OH, with no observation of removal of its reaction partner (CS_2 or OCS) or of formation of the stable product (OCS or CO_2). No direct evidence exists for rearrangments in the sulfur systems of the kind proposed for (1) and (2) (Kurylo, 1978; Cox and Sheppard, 1980), but a similar rearrangement has been suggested to explain the observed isotopic scrambling of ^{18}O in the reaction of ^{18}OH with CO_2 (Kurylo and Laufer, 1979).

We have sought confirmation of the formation of OCS in the reaction of OH with CS_2, as required by (1), through direct product analysis. Our experiments have been carried out with radioactive $^{14}CS_2$, assaying for $O^{14}CS$ by radio gas

TABLE 1. Measurements of the Rate Constant for the Reaction of OH with CS_2 to Form O=C=S

Authors	Rate Constant cm^3 $molecule^{-1}$ sec^{-1}
Atkinson et al., 1978	$< 7 \times 10^{-14}$
Kurylo, 1978	$18.5 \pm 3.4 \times 10^{-14}$
Cox and Sheppard, 1980	$43 \pm 16 \times 10^{-14}$
Wine et al., 1980	$< 0.15 \times 10^{-14}$
This work	$< 0.3 \times 10^{-14}$

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chromatography (Wolfgang and Rowland, 1958; Lee et al., 1962). The OH radicals were formed by 254 nm irradiation of H_2O_2 in a system containing about 1-2 torr of H_2O_2; small quantities (1-20 torr) of CO, C_3H_8 or iso-C_4H_{10}; and 60-80 torr of $^{14}CS_2$. The overall flux of OH was monitored through the observation of CO_2 formation from the oxidation of CO as in (5), or through diminution in concentration of the hydrocarbon by reaction (6). The rate constants for these reactions are

$$OH + CO \rightarrow CO_2 + H \qquad (5)$$

$$OH + RH \rightarrow H_2O + R \qquad (6)$$

all convenient for relative measurements of reactions competing with (1) if the latter is proceeding at the rapid rates reported by Kurylo (1978) or by Cox and Sheppard (1980). Our analytical technique is capable of detecting the formation of about 1 part in 10^5 of $O^{14}CS$ in $^{14}CS_2$, and of course OCS formed from any other carbon source would not be labeled with ^{14}C. Earlier laboratory experiments have shown that the molecule OCS can be readily formed under experimental conditions in which both S atoms and CO are present in minuscule concentrations (Lee et al., 1964).

Experimental

Chemicals. Hydrogen peroxide was concentrated to > 95% by room temperature distillation of 90% aqueous H_2O_2 (FMC Corporation), followed by storage at 77K. The radioactive $^{14}CS_2$ was obtained from Amersham with a specific radioactivity of 55 mCi/mmole, and diluted with chromatoquality CS_2 (Matheson, Coleman and Bell) to a specific activity of 24 μCi/mmole. This mixture contained $O^{14}CS$ as an impurity (0.07% of total ^{14}C activity) and was therefore purified by preparative gas chromatography. The CS_2 + $^{14}CS_2$ mixture (designated below as $*CS_2$) used in photolysis contained < 0.001% each of the total ^{14}C in the forms of ^{14}CO, $^{14}CO_2$ and ^{14}OCS. Carbon monoxide (Matheson Research grade) was purified by passage through a glass bead trap at 77K. The other gases were used as furnished: C_3H_8, Matheson, Instrumental Grade; iso-C_4H_{10}, Phillips Research Grade.

Light Sources and Photolysis Cells. Two photolysis arrangements were used. The initial experiments were carried out in a 170 cm^3 quartz photolysis cell with suprasil windows, and a 1000-watt Xenon Mercury arc lamp operated through a Bausch & Lomb monochromator for irradiation at 254 nm. All of the experiments listed in Table 2 were performed with a 207 cm^3 Vycor 791 cell and an Ultraviolet Products Mineralight R-52 lamp for higher intensity at 254 nm.

Analytical Procedure. After 3-6 hours of photolysis, the samples containing CO, $*CS_2$ and H_2O_2 were cooled to 77K, and CO (plus O_2 formed during photolysis) were transferred to a silica gel chromatographic loop at 77K. The fraction condensible at 77K was then analyzed by radio gas chromatography (Lee et al., 1962; Iyer, 1973) on a 5-foot Chromosorb-102 column which separated CO_2, OCS and CS_2 in that order. After the elution of the OCS peak, the flow stream was diverted through a glass bead trap at 77K to prevent proportional counter contamination from the very highly radioactive $*CS_2$. The $^{14}CS_2$ content was separately assayed with a small aliquot, normally containing only about 1/20 of the sample. The contents of the silica gel loop were analyzed on a 20-foot charcoal column which separates CO from O_2 and N_2.

Similar procedures were used for samples containing iso-C_4H_{10} or C_3H_8 in place of CO. The Chromosorb column was operated at 333K for the separation of OCS from C_3H_8, and at 358K for the separation of iso-C_4H_{10} and OCS.

A typical filling of the cell to 50 torr pressure of $*CS_2$ corresponded to approximately 4 x 10^6 counts min^{-1} measured at a flow rate of 30 ml per minute through the counter.

Results

For each experiment, a percentage conversion of $^{14}CS_2$ to $O^{14}CS$ can be measured and compared with the percentage change of CO to CO_2 or percentage removal of RH. Typical data for all three of these types of experiments are summarized in Table 2. In each case, the presence of other oxidized forms of ^{14}C (^{14}CO and $^{14}CO_2$) demonstrates that a variety of chemical reactions are occurring in these photolysis systems, and the observation of $O^{14}CS$ therefore does not demonstrate that reaction (1) must be occurring, since other reaction routes could be forming $O^{14}CS$ as well as ^{14}CO and $^{14}CO_2$. Macroscopic amounts of CO_2 and OCS were always observed as well. The experimental observations of yields of $O^{14}CS$ are converted into upper limits for the absolute rate constant for k_1 through the known reaction rate constants for k_5 (NASA, 1979) and k_6 (Gorse and Volman, 1974; Butler et al., 1978).

Discussion

Our experiments have consistently shown that $O^{14}CS$ is not formed by the reaction of OH with $^{14}CS_2$ at any rate comparable to the rates reported by Kurylo (1978) and by Cox and Sheppard (1980). A conservative upper limit from six separate experiments with CO as the monitor at 298K is $k_1 < 0.3 \times 10^{-14}$ cm^3 $molecule^{-1}$ sec^{-1}, with one experiment at 313K putting the limit at 0.1 x 10^{-14} cm^3 $molecule^{-1}$ sec^{-1}. Equivalent results were obtained with both light sources. The experiments with C_3H_8 and iso-C_4H_{10} as monitors also show k_1 to be much less than measured by Kurylo (1978) and by Cox and Sheppard (1980). In all cases, other chemical processes than (1) are possible leading to the formation of $O^{14}CS$, so that there is no requirement that k_1 be other than zero. Since reaction (4) is endothermic, our upper limit on k_1 is also an upper limit for the overall reaction rate of OH with CS_2. The insertion of this upper limit into various atmospheric models leads to the conclusions that: (a) CS_2 is not an important precursor for OCS in the atmosphere; and (b) reaction with OH is not an important route for the removal of CS_2 from the earth's atmosphere.

Several of the experimental measurements summarized in Table 1 are based upon comparative OH removal rates in the absence and presence of added CS_2 during the flash photolysis of H_2O, without measurement of concentration changes for

TABLE 2. Typical Experimental Results in the 254 nm Photolysis of H_2O_2-CS_2 Mixtures

Pressure, torr					
H_2O_2	0	0.9[a]	1.4	1.8	1.8
*CS_2	53.4	50.2	53.6	70.1	66.1
CO	20.1	18.6	20.0	0	0
C_3H_8	0	0	0	2.0	0
iso-C_4H_{10}	0	0	0	0	1.7
Observed Radioactivity in Product, % of Total ^{14}C					
^{14}CO	0.084	0.936	2.09	(n.m.)	0.589
$^{14}CO_2$	0.006	0.069	0.63	0.118	0.053
$O^{14}CS$	0.009	0.021	0.15	0.106	0.066
%CO → CO_2	1.2	3.1	7.9	-	-
%RH removed	-	-	-	18.3	17.4
Δ(Monitor)/Δ(OCS)					
k_5/k_1	-	150	50	-	-
k_6/k_1	-	-	-	170	260
k_1, 10^{-14} cm^3 $molecule^{-1}$ sec^{-1}		⩽ 0.1	⩽ 0.3	⩽ 0.9	⩽ 0.8

(a) Temperature 313K for this experiment; others at 298K.
k_5 = 1.5 x 10^{-13} cm^3 $molecule^{-1}$ sec^{-1} (NASA, 1979) at 0.1 atmosphere.
k_6 = 1.6 x 10^{-12} cm^3 $molecule^{-1}$ sec^{-1} (Butler et al., 1978) for i-C_4H_{10}.
k_6 = 2.2 x 10^{-12} cm^3 $molecule^{-1}$ sec^{-1} (Gorse and Volman, 1974) for C_3H_8.
n.m. = not measured

CS_2, OCS or SH. These photolytic systems also involve the photodecomposition of CS_2 when it is present, with the release of S atoms. The relative extent of photolysis of CS_2 versus the OH source was lowest in the experiments of Wine et al., (1980), who observed essentially no increase in OH removal rate with added CS_2.

We believe that plausible alternate mechanisms exist for the increased disappearance rate for OH found by Kurylo (1978) and for CS_2 by Cox and Sheppard (1980), including the possibility of OH reaction with fragments from CS_2 photolysis, i.e., OH + S and OH + CS. The latter combination may be the pathway by which $O^{14}CS$ is formed in our experiments, and for the OCS found by Cox and Sheppard.

The use of a very different kinetic measurement technique in our experiments has the advantage that our sensitivities to impurities are unlike those encountered in flash-photolysis OH-disappearance measurements. In particular, the reaction of OH with trace levels of H_2S has no important consequence in our system, except a lowering of the concentration of OH radicals available for reactions (1), (5) and (6). Since no ^{14}C is involved in that reaction, no $O^{14}CS$ can be formed. On the other hand, the reaction of OH with H_2S with a rate constant of 3 x 10^{-12} cm^3 $molecule^{-1}$ sec^{-1} (NBS, 1977) is sufficiently rapid that an H_2S/CS_2 ratio of 10^{-3} in a flashed CS_2/H_2O mixture can explain an apparent rate constant of 3 x 10^{-15} cm^3 $molecule^{-1}$ sec^{-1} for the disappearance of OH in a CS_2 system.

While we have not performed any experiments here which relate to the reaction of OH with OCS, the positive evidence for reaction (2) and/or (3) with OCS has been obtained by Kurylo (1978) by the same technique used for gathering the CS_2 data of Table 1. With OCS as the reactant for OH, Cox and Sheppard have reported that essentially no reaction is observed, in marked contrast to their results with CS_2. Wine et al., (1980) have also reported that no rapid reaction is observed. We conclude that the reaction of OH with OCS in all probability does not proceed at a rapid rate, and therefore that: (a) reaction with OH is not an important tropospheric sink for OCS; and (b) OCS is not an important tropospheric precursor of SO_2. The ultraviolet photolysis of OCS in the stratosphere can be a source of SO_2 through the subsequent reactions of the atomic S released during photodecomposition (Crutzen, 1976).

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